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Description

The present invention relates to bleach compositions. In particular, it relates to thickened bleach compositions and the method of thickening them.

Bleach compositions are typically aqueous solutions of alkali metal and alkaline earth metal hypochlorites. They are useful as cleaning agents, disinfectants, bactericides and fungicides. For example, bleach compositions are useful for cleaning textiles, dishes and glassware; and sinks, bathtubs and numerous other porcelain items.

Bleach compositions contain mostly water and therefore have viscosities similar to water. Unfortunately, it is often necessary to apply bleach compositions to vertical or inclined surfaces. Because the composition has low viscosity, it will not adhere to a vertical or inclined surface. A thickened bleach composition which could be easily applied, for example by spraying, and could adhere to a vertical or inclined surface without dripping would be desirable. Thickened bleach compositions are disclosed in U.S. Patent Nos. 4,388,204; 4,390,448; EPO Publication No. 110,544 and British Patent No. 1,466,560. The bleach compositions of the references use various detergents or surface-active agents to thicken the composition. However, no one- or two-component surfactant additive system has been proven satisfactory with regard to phase stability, bleach stability, and viscosity stability. Therefore, it would be desirable to provide a thickened bleach composition that employs only a one- or two-component additive system and exhibits good phase stability and bleach stability, as well as viscosity stability.

Bleach compositions are often applied to numerous items using dispensers like the manually operated atomizing dispensers disclosed in U.S. Patent No. 4,463,905. Unfortunately, when typical bleach compositions are employed as a spray using such a dispenser, they can form an undesirable mist. This mist can cause problems if the vapors are inhaled, since the vapors can be disagreeably strong, as well as injurious to health. In addition, the mist can drift undesirably onto unprotected surfaces. For example, it can come into contact with clothing and other fabrics, skin and eyes. Therefore, it would be desirable to provide a thickened bleach composition that can be employed as a substantially nonmisting spray while still maintaining its stability.

In one aspect, the present invention is a method for thickening an aqueous bleach composition containing a bleaching agent comprising forming a viscoelastic surfactant therein by contacting the composition with an effective amount of a surfactant ion having a hydrophobic moiety chemically bonded to an ionic, hydrophilic moiety and of an electrolyte having a moiety that associates with the surfactant ion to form a viscoelastic surfactant and, optionally, further thickening the bleach composition and/or increasing its viscosity stability at higher temperatures by adding a further amount of an electrolyte having a moiety that associates with the surfactant ion.

In another aspect, the present invention is a thickened aqueous bleach composition made according to the method described above comprising a bleaching agent, surfactant ions and counterions, and water; the components of the composition being combined to form an aqueous solution under suitable solution conditions whereby the surfactant ions and counterions associate in the bleach composition thereby forming a viscoelastic surfactant.

The addition of excess counterions to the bleach composition in accordance with the practice of this invention can further increase its viscosity, increase its viscosity stability at higher temperatures, or both.

The thickened bleach compositions of this invention are useful because they exhibit good phase stability, bleach stability, and viscosity stability, and they will adhere to a vertical or inclined surface without dripping. They are also useful because they can be employed as a substantially non-misting spray.

This invention allows the skilled artisan to produce a thickened bleach composition. It also allows the skilled artisan to apply the composition in the form of a spray to a surface by expelling the composition from a dispensing device. The thickened or gelled bleach composition can be expelled from the dispenser easily despite its thickened character because the composition is thickened with a viscoelastic surfactant that can provide a shear thinning behavior. Because the viscoelastic surfactant is also shear stable, it also allows the bleach composition to thicken after it is expelled from the dispenser, as for example, when the composition is applied to a surface. Therefore, the bleach composition can be applied to a vertical surface without substantial running or dripping. In addition, the bleach composition can be applied in the form of a stream or spray to a surface without the formation of an undesirable mist as the composition is expelled from a dispenser.

As used herein, the term "bleach composition" refers to an aqueous liquid that contains a bleach active agent. Such agents include hydrogen peroxide, potassium perchlorate, sodium hypochlorite, sodium peroxide, sodium chlorite, calcium hypochlorite (i.e., chlorinated lime), sodium hypobromite, and iodine nonionic surfactant complexes. Typically, bleach compositions range from 0.5 to 50, preferably from 1 to 10

weight percent bleaching agent and from 50 to 99.5, preferably from 90 to 99, weight percent aqueous liquid. The concentration of bleaching agent required will depend on the bleaching agent employed.

The term "aqueous liquid" refers to liquids which contain water. Included herein are substantially pure water, water containing inorganic salts, and aqueous alkaline and acidic solutions. Aqueous liquids include mixtures of water and water-miscible liquids, provided that the concentration of water-miscible liquids does not adversely affect the stability of the bleach composition or the viscoelastic properties of the aqueous liquid. Also included herein are emulsions of immiscible liquids in water, and sprayable aqueous slurries of small sized solid particulates. Therefore, the aqueous liquids of this invention can contain fine particulate bentonites, silica, and/or calcium carbonate. Water, water containing inorganic salts and aqueous alkaline, and acidic solutions are preferred. Most preferred is an aqueous alkaline solution wherein the total electrolyte concentration is less than 25, preferably less than 10, weight percent of the aqueous liquid.

The aqueous liquid of this invention need not contain gritty materials, which are undesirable in some applications, to thicken the bleach composition. For example, gritty materials can be difficult to adequately remove from certain surfaces.

The term "mist" as it applies to aqueous liquids, means fine liquid droplets suspended in or falling through a moving or stationary gas atmosphere. Specifically, a mist provides an undesirable drift of aqueous droplets through a gas atmosphere. The properties of a mist, and tests to determine such properties are well known in the art and reference is made to Perry and Chilton, *Chemical Engineer's Handbook*, 5th Ed., Vol. 18, McGraw-Hill (1973). In distinguishing a mist from a spray, a mist is generally defined as a gas-suspended liquid particle which has a diameter of less than 10 μm , while a spray is a gas-suspended liquid particle which has a diameter of greater than 10 μm . However, it is understood that the specific size of spray and mist particles may vary depending upon the industrial use such as where a controlled droplet size is desired. As used herein, the terms "antimisting" and "non-misting" as applied to an aqueous liquid refers to the property which comprises the tendency of said liquid to not form a mist, i.e., undersized droplets that are easily gas-suspended.

The terms "dispenser" and "dispensing device" refer to devices which can provide a stream or spray of the bleach composition as defined herein. Typically, the dispenser is a hand-held device. For example, the dispensing device can include a container for the bleach composition, a pump, and a spray-forming or stream-forming nozzle. The pump ejects the bleach composition from the container, through the nozzle, and into the atmosphere. Examples of suitable dispensing devices are disclosed in U.S. Patent Nos. 4,463,905; 3,572,590; 3,985,271; 2,826,399; 4,013,228 and 4,153,208. The preferred dispensing devices have parts that are resistant to chemical attack by bleach. They also can include a suitable aerosol device that has a propellant, an atomizer, or both. Preferably, the aerosol device is one which forms a spray when employed.

Traditionally, engineers and scientists have been concerned with two separate and distinct classes of materials - the viscous fluid and the elastic solid. The simple linear engineering models, Newton's law for flow and Hooke's law for elasticity, worked well because most traditional materials (e.g., water, motor oil, and steel) fell in one of these two categories. However, as polymer science developed, scientists realized that these two categories represented only the extremes of a broad spectrum of material properties, and that polymers fell somewhere in the middle. As a result, polymer melts and solutions were characterized as "viscoelastic". The term "viscoelastic" refers to polymers that exhibit a combination of viscous (liquid-like) and elastic (solid-like) properties.

The phenomenon of viscoelasticity has been discovered in certain aqueous surfactant solutions. Surfactants consist of molecules containing both polar and non-polar groups. They have a strong tendency to adsorb at surfaces or interfaces and thereby lower the surface or interfacial tension. Solutions of surfactants also form micelles, which are organized aggregates of the surfactants. A selected group of surfactant solutions also impart viscoelasticity to the solution as well. (See. S. Graysholt, J. Coll. and Interface Sci., 57, (3) pp. 575-6 (1976), for a study of various surfactant compositions that impart viscoelasticity to aqueous solutions). However, typical surfactant compositions will not inherently possess viscoelastic properties. As reported in H. Hoffmann, *Advances in Coll. and Interface Sci.*, 17 pp. 276 (1982), surfactant compositions that impart viscoelastic properties to solutions are rare. Therefore, although all surfactant compositions will reduce surface tension, few will impart viscoelasticity. Those that do are known as "viscoelastic surfactants", and they possess desirable properties. It has been discovered that viscoelastic surfactants can be added to a water-based heat transfer fluid to improve its performance (U.S. Patent 4,534,875).

Viscoelasticity is caused by a different type of micelle formation than the usual spherical micelles formed by most surfactant compositions. Viscoelastic surfactants form rod-like or cylindrical micelles. Although cylindrical micelles and spherical micelles have about the same diameter of 50 \AA (0.005 μm), cylindrical micelles can reach 1,000 to 2,000 \AA (0.1 to 0.2 μm) in length and contain hundreds or thousands

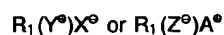
of individual surfactant molecules. This high degree of association requires a specific set of conditions that can only be achieved by matching the surfactant composition with a suitable solution environment. The solution environment will depend on factors such as the type and concentration of electrolyte and the structure and concentration of organic compounds present. Therefore, a surfactant composition may form cylindrical micelles in one solution to impart viscoelastic properties to it and form spherical micelles in another solution. The solution with spherical micelles will exhibit normal surfactant behavior and will not exhibit viscoelasticity. A determination of whether a solution is viscoelastic can be easily determined by empirical evaluation as described hereinafter.

The formation of long, cylindrical micelles in viscoelastic surfactants creates useful rheological properties. First, viscoelastic surfactants exhibit reversible shear thinning behavior. This means that under conditions of high stress, such as when the composition is sprayed through a nozzle, the composition will exhibit low viscosity. When the conditions of high stress are replaced with conditions of low stress, such as obtained when the composition has left the nozzle and is only subjected to gravitational force as it resides on a vertical surface, the composition will exhibit high viscosity. Secondly, viscoelastic surfactants will remain stable despite repeated high shear applications. Therefore, the thickened composition can be sprayed efficiently from a dispenser without undesirable mist and yet maintain its integrity on a vertical wall without running or dripping. Since typical polymeric thickeners will degrade when subjected to high shear, a bleach composition thickened with such a polymer will lose its integrity after repeated shearing.

The major test specified by the references discussed above to determine if an aqueous solution possesses viscoelastic properties consists of swirling the solution and visually observing whether the air bubbles created by the swirling recoil after the swirling is stopped. This has been the traditional test for many years. It is possible to quantify the degree of viscoelasticity a solution possesses by measuring the time required for the recoil motion to stop, as described in an article by J. Nash, *J. of Appl. Chem.*, 6, pp. 540 (1956).

The surfactant compositions within the scope of this invention are ionic viscoelastic surfactants. The proper choice of counterion structure and solution environment gives viscoelasticity. It has been discovered that certain viscoelastic surfactants will thicken a bleach composition without unduly sacrificing bleach stability. What follows is a discussion of ionic surfactant compounds and the counterions necessary to impart viscoelasticity to bleach compositions.

In general, ionic surfactant compounds comprise an ionic, hydrophilic moiety chemically bonded to a hydrophobic moiety (herein called a surfactant ion) and a counterion sufficient to satisfy the charge of the surfactant ion. Examples of such surfactant compounds are represented by the formula:



wherein $R_1(Y^{\circ})$ and $R_1(Z^{\circ})$ represent surfactant ions having a hydrophobic moiety represented by R_1 and an ionic, solubilizing moiety represented by the cationic moiety Y° or the anionic moiety Z° chemically bonded thereto. X° and A° are the counterions associated with the respective surfactant ions.

In general, the hydrophobic moiety (i.e., R_1) of the surfactant ion is a hydrocarbyl or inertly substituted hydrocarbyl radical having one or more substituent groups, e.g., halo groups such as -F, -Cl, or -Br or chain linkages, such as silicon linkage (-Si-), which are inert to the aqueous liquid and components contained therein. Typically, the hydrocarbyl radical is an aralkyl group or a long chain alkyl or inertly substituted alkyl, which alkyl groups are generally linear and have at least 12 carbon atoms. Representative long chain alkyl groups include dodecyl (lauryl), tetradecyl (myristyl), hexadecyl (cetyl), octadecyl (stearyl) and the derivatives of tallow, coco and soya. Preferred groups are generally alkyl groups having from 14 to 24 carbon atoms, with octadecyl, hexadecyl, and tetradecyl being the most preferred.

The cationic, solubilizing hydrophilic moieties or groups, i.e., Y° , are generally onium ions wherein the term "onium ions" refers to a cationic group which is essentially completely ionized in water over a wide range of pH, e.g., pH values of from 2 to 13. Representative onium ions include, for example, quaternary ammonium groups, i.e., $-N^{\circ}(R)_3$; tertiary sulfonium groups, i.e., $-S^{\circ}(R)_2$; and quaternary phosphonium groups, i.e., $-P^{\circ}(R)_3$, wherein each R is individually a hydrocarbyl or inertly substituted hydrocarbyl. Of such cationic groups, the surfactant ion of the viscoelastic surfactant is preferably prepared having a quaternary ammonium group, i.e., $-N^{\circ}(R)_3$, with each R preferably being methyl or ethyl.

Representative anionic, solubilizing hydrophilic moieties or groups, herein designated Z° , include sulfate groups, ether sulfate groups, sulfonate groups, carboxylate groups, phosphate groups, and phosphonate groups. Of such anionic groups, the surfactant ion of the viscoelastic surfactants is preferably prepared having a carboxylate or sulfate group. The most preferred anionic surfactant ion is an alkyl diphenyl ether disulphonate sold by The Dow Chemical Company, under the trademark "DOFAX 2A1", especially where

the alkyl group is octadecyl.

Fluoroaliphatic species suitably employed in the practice of this invention include organic compounds represented by the formula:



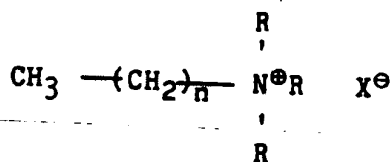
wherein R_f is a saturated fluoroaliphatic moiety, preferably containing a F_3C- moiety and Z^1 is an ionic moiety. The fluoroaliphatics can be perfluorocarbons. Suitable ionic moieties will be described hereinafter. The fluoroaliphatic moiety advantageously contains from 3 to 20 carbons wherein all can be fully fluorinated, preferably from 3 to 10 of such carbons. This fluoroaliphatic moiety can be linear, branched or cyclic, preferably linear, and can contain an occasional carbon-bonded hydrogen or halogen other than fluorine. More preferable are those linear perfluoroaliphatic moieties represented by the formula: $C_n F_{2n+1}$ wherein n is in the range of from 3 to 10. An example of a linear perfluorocarbon that is stable to oxidation is $CF_3(CF_2)_p SO_3^- A^+$ wherein p is from 2 to 6. The method of its preparation is described in U.S. Patent 2,732,398.

The counterions (i.e., X^- or A^+) are ions that have a charge opposite that of the surfactant ions. The counterions and surfactant ions associate in the bleach composition and impart viscoelastic properties to it. Ions that are anionic serve as counterions for surfactant ions having a cationic hydrophilic moiety; and the ions that are cationic serve as counterions for surfactant ions having an anionic, hydrophilic moiety. The organic counterions are formed by dissociation of the corresponding salts, acids, or bases.

The preferred anionic counterions are organic, especially sulfonates or carboxylates. Representative of such anionic counterions which, when employed with a cationic surfactant ion, are capable of imparting viscoelastic properties to the bleach composition include various aromatic sulfonates such as p-toluene sulfonate and naphthalene sulfonate; and chlorobenzoic acid, where such counterions are water-soluble. Most preferred are p-toluene sulfonate, 3,4-dichlorobenzoate, and an alkyl diphenyl ether disulphonate sold by The Dow Chemical Company, under the trademark "DOFAX 2A1", especially where the alkyl group is octadecyl.

The cationic counterion may be an onium ion, most preferably a quaternary ammonium group. Representative cationic counterions in the form of a quaternary ammonium group include benzyl trimethyl ammonium or alkyl trimethyl ammonium wherein the alkyl group is advantageously octyl, decyl, dodecyl and cetyl. Most preferred is an alkyltrimethylammonium such as hexadecyltrimethylammonium supplied in the form of the bromide (HTAB). It is highly desirable to avoid stoichiometric amounts of surfactant ions and counterions when the alkyl groups of the counterions are large. The use of cationic counterions is generally less preferred than the use of anionic counterions.

The particular surfactant ions and counterions are selected so that the combination imparts viscoelastic properties to an aqueous liquid. Of the aforementioned surfactant ions and counterions, those combinations which form such viscoelastic surfactants will vary but are easily determined by the test methods hereinbefore described. Of the surfactant compounds which impart viscoelastic properties to an aqueous liquid, the preferred surfactant compounds include those represented by the formula:



wherein n is an integer from 13 to 23, preferably an integer from 15 to 21; each R is independently an alkyl group, or alkylaryl, preferably independently methyl, ethyl or benzyl; and X^- is a p-toluene sulfonate. Especially preferred surfactant ions include cetyltrimethylammonium, myristyltrimethylammonium, and octadecyltrimethylammonium. Combinations of surfactant compounds can also be employed.

The viscoelastic surfactants are easily prepared by admixing the basic form of the desired cationic surfactant ions with a stoichiometric amount of the acidic form of the desired anionic counterions or by admixing the acidic form of the desired anionic surfactant ions with a stoichiometric amount of the basic form of the desired cationic counterions. Alternatively, stoichiometric amounts of the salts of the surfactant ions and counterions can be admixed to form the viscoelastic surfactant. See, for example, the procedures

described in U.S. Patent 2,541,816. Once the viscoelastic surfactant is prepared, the thickened bleach composition is prepared by admixing the viscoelastic surfactant with the bleach composition.

The concentration of viscoelastic surfactant required to impart viscoelastic properties to the bleach composition, where the viscoelasticity is measured by the techniques previously described, is that which measurably increases the viscosity of the composition. The type and concentration of viscoelastic surfactant required to increase the viscosity depends on the composition of the aqueous liquid, temperature, shear rate to which the bleach composition will be subjected, and the end use contemplated. In general, the requisite concentration of any specific viscoelastic surfactant is determined experimentally. Preferably, the concentration of viscoelastic surfactant ranges from 0.05 to 10 weight percent of the bleach composition. More preferably, the concentration of viscoelastic surfactant ranges from 0.1 to 2 weight percent of the bleach composition.

In a preferred embodiment of this invention, excess counterions are added to the bleach composition to further increase its viscosity, increase its viscosity stability at higher temperatures, or both. The counterions employed will have a charge opposite that of the surfactant ions and will dissolve in the bleach composition. Preferably, the excess counterions employed are the same as the counterions employed to associate with the surfactant ions to form the viscoelastic surfactant. However, the excess counterions can be different from the counterions which form the viscoelastic surfactant.

The concentration of excess counterions required to further increase the viscosity, increase the stability at higher temperatures, or both, will depend on the composition of the aqueous liquid, the surfactant ions and counterions employed, and the desired viscosity. Ordinarily, the concentration of excess counterions which will produce a noticeable effect ranges from 0.1 to 20, and more assuredly and preferably from 0.5 to 5, moles per mole of surfactant ions.

The bleach composition may contain an emulsion of an immiscible liquid, such as an oil or other organic ingredient, at a concentration ranging from 0.05 to 20 weight percent of the bleach composition. However, the concentration of immiscible liquid must be lower than that which will adversely affect the stability of the bleach composition. Viscoelastic surfactants employed in such emulsions tend to lose their viscoelasticity, possibly because the oil penetrates the micelles and destroys the aggregates required for viscoelasticity. Viscoelastic surfactants containing excess counterions maintain viscoelasticity in an emulsion longer than those without the excess counterions. Moreover, fluorinated viscoelastic surfactants maintain viscoelasticity in an emulsion longer at concentrations ranging up to 50 weight percent, most preferably up to 10 weight percent of the bleach composition.

The bleach compositions of this invention exhibit good bleach stability, phase stability, and viscosity stability. Good bleach stability refers to a thickened bleach composition that experiences less than 10 percent bleach degradation, which is the loss of the bleach active agent, for more than 30 days when stored under atmospheric conditions in a clear container in the dark at 30 °C. Good viscosity stability refers to a bleach composition that exhibits a viscosity at room temperature greater than 600 cps (0.6 Pa.s) when subjected to a shear rate less than 5 sec⁻¹, more than 30 days after the composition is formulated and stored using the test conditions above. Good phase stability refers to the lack of development of separate phases for the bleach composition and viscoelastic surfactant until the bleach activity falls below useful values (for example, 75 percent bleach degradation).

If desired, the bleach composition can be a foam, which is a thickened liquid having a dispersion of gas therein. For example, the bleach composition can be vigorously agitated prior to use as a spray or stream. In addition, a surfactant, or other foam forming material can be used as an additive. Furthermore, a fine mesh screen device can be fitted over the nozzle of the dispensing device to intercept emitted bleach composition.

The following examples are presented to further illustrate but not limit the scope of this invention. All parts and percentages are by weight unless otherwise indicated.

Example I and Comparative Run A

To 71.43 grams (g) of a commercially available NaOCl bleach formulation, sold by Gibraltar National Corporation under the trademark "ROMAN BLEACH", which contained an aqueous liquid and 5.6 percent active NaOCl was added 27.45 g distilled water. To this solution was added 0.73 g hexadecyltrimethylammonium bromide and 0.39 g sodium p-toluene sulfonate. The mixture was agitated to the point at which a uniform viscoelastic solution resulted.

The sample was transferred to a polyethylene bottle which was sealed and placed in a constant temperature (31 °C) dark environment. Portions of the sample were periodically removed in order to evaluate the NaOCl concentration. The amount of NaOCl was determined using titration techniques

employing sodium thiosulfate and starch/iodine indicator. Viscosity of the thickened bleach compositions were periodically evaluated using a Rheometrics Fluids Rheometer in a steady shear mode, and cone and plate configuration. Data are presented in Table I.

TABLE I

[illegible]

N.M. indicates that the viscosity of the composition is not measured, but the viscosity of the sample approximately equals that of an unthickened aqueous liquid (i.e., about 1 cp).

The data in Table I illustrate that the thickened formulation of this invention is shear thinning and

exhibits excellent bleach stability over time as well as acceptable high viscosity stability. Conversely, a similar bleach composition thickened with 1 percent sodium polyacrylate rather than a viscoelastic surfactant (Comparative Run A) experienced 84 percent reduction in viscosity after 18 days of similar treatment conditions. This is an unacceptably high rate of loss of thickening activity.

Example 2

To 178.57 g of a commercially available NaOCl bleach formulation, sold by Gibraltar National Corporation under the Trademark "ROMAN BLEACH", which contained an aqueous liquid and 5.6 percent active NaOCl was added 166.45 g deionized water. To this solution was added 2.50 g hexadecyltrimethylammonium bromide and 2.50 g sodium p-toluene sulfonate.

The sample was transferred into a dispensing device which is generally described in U.S. Patent No. 4,463,905. The screen in front of the nozzle was removed. A portion of the sample was sprayed onto a greasy vertical enamel painted surface and was observed to provide a good distribution of spray which uniformly covered the surface. The treated surface was cleaned by the sprayed bleach sample. The sample which was sprayed onto the vertical metallic surface was observed to adhere to said surface for several minutes (i.e., 10 minutes) without a substantial amount of dripping occurring. The screen in front of the nozzle was reattached to the dispensing device. A portion of the sample was sprayed onto the vertical glass surface as described hereinbefore. The sample which was sprayed onto the vertical glass surface formed a white, non-transparent, fairly thick foam; which foam adhered to the surface for several minutes (i.e., 10 minutes) without the occurrence of substantial amounts of dripping. The sample in all three instances was applied as a spray wherein the dispensing device was operated without greater effort than was required for the spraying of essentially pure water. The bleach composition which was sprayed on the aforementioned surfaces was rinsed from the surface using water and no visible film remained on the surfaces.

Example 3

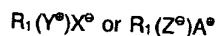
A thickened bleach composition was prepared using the formulation and procedure of Example 1, except that sodium 3,4-dichlorobenzoate was substituted in an equimolar amount for sodium p-toluene sulfonate. The sample was transferred to a polyethylene bottle which was sealed and placed in a constant temperature (31 °C) dark environment. Samples of the composition were periodically evaluated using the techniques of Example 1. Data are presented in Table II.

Percent of Original NaOCl Remaining After:	Viscosity of Composition, cp (Pa·s), when subjected to Shear Rate of 0.631 sec ⁻¹ After:					
	<u>7 days</u>	<u>35 days</u>	<u>70 days</u>	<u>24 hrs.</u>	<u>7 days</u>	<u>35 days</u>
	100	87.8	62.3	3020(3.02)	2780(2.78)	1000(1.00)

The data in Table II illustrate that carboxylate counterions can replace sulphonate counterions to form a viscoelastic surfactant. The bleach composition thickened with the viscoelastic surfactant exhibited excellent bleach stability and viscosity stability over time.

Claims

1. A method for thickening an aqueous bleach composition containing a bleaching agent, comprising forming a viscoelastic surfactant therein by contacting the composition with an effective amount of a surfactant ion having a hydrophobic moiety chemically bonded to an ionic, hydrophilic moiety and of an electrolyte having a moiety that associates with the surfactant ion to form a viscoelastic surfactant and, optionally, further thickening the bleach composition and/or increasing its viscosity stability at higher temperatures by adding a further amount of an electrolyte having a moiety that associates with the surfactant ion.
2. A method as claimed in Claim 1, wherein said viscoelastic surfactant is represented by the formula:



5 wherein $R_1(Y^\oplus)$ and $R_1(Z^\ominus)$ represents surfactant ions, R_1 is a hydrophobic moiety, Y^\oplus is a cationic solubilizing hydrophilic moiety chemically bonded to R_1 , Z^\ominus is an anionic solubilizing hydrophilic moiety chemically bonded to R_1 , X^\ominus is a counterion associated with Y^\oplus and A^\oplus is a counterion associated with Z^\ominus .

10 3. A method as claimed in Claim 2, wherein the surfactant ion is represented by the formula



wherein R_1 and X^\ominus are as defined in Claim 2, and Y^\oplus is an onium ion.

15 4. A method as claimed in Claim 3, wherein Y^\oplus is selected from quaternary ammonium, sulfonium and phosphonium groups.

5. A method as claimed in Claim 4, wherein Y^\oplus is a quaternary ammonium group of the formula $N^\oplus(R)_3$, wherein each R is methyl or ethyl.

20 6. A method as claimed in Claim 2, wherein the surfactant ion is represented by the formula



25 wherein R_1 and A^\oplus are as defined in Claim 2, and Z^\ominus is selected from sulfate groups, ether sulfate groups, sulfonate groups, carboxylate groups, phosphate groups and phosphonate groups.

7. A method as claimed in Claim 6, wherein Z^\ominus is selected from carboxylate groups and sulfate groups.

30 8. A method as claimed in any one of Claims 2 to 7, wherein R_1 represents a C_{14} - C_{24} alkyl group.

9. A method as claimed in Claim 8, wherein said surfactant ion is selected from cetyltrimethylammonium, myristyltrimethylammonium and stearyltrimethylammonium.

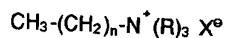
35 10. A method as claimed in any one of the preceding claims, wherein the hydrophobic moiety contains a fluoroaliphatic group.

40 11. A method as claimed in Claim 10, wherein said fluoroaliphatic group is a linear perfluoroaliphatic group represented by the formula C_nF_{2n+1} , wherein n is 3 to 10.

12. A method as claimed in any one of Claims 1 to 5 and 8 to 11, wherein the counterion to the surfactant ion in the viscoelastic surfactant is a sulfonate or carboxylate.

45 13. A method as claimed in Claim 12, wherein the counterion is an aromatic sulfonate.

14. A method as claimed in Claim 13, wherein the viscoelastic surfactant is represented by the formula



50 wherein n is 13 to 23, each R independently is alkyl or alkylaryl and X^\ominus is p-toluene sulfonate.

15. A method as claimed in any one of Claims 1, 2 and 6 to 11, wherein the counterion to the surfactant ion in the viscoelastic surfactant is an onium ion.

55 16. A method as claimed in Claim 15, wherein the counterion is a quaternary ammonium group.

17. A method as claimed in any one of the preceding claims, wherein said viscoelastic surfactant is present in an amount of from 0.05 to 10 percent based on the weight of the bleach composition.

18. A method as claimed in Claim 17, wherein said amount is 0.1 to 2 weight percent.

19. A method as claimed in any one of the preceding claims, wherein said optional further amount of electrolyte is added to the viscoelastic surfactant-containing bleach composition.

20. A method as claimed in Claim 19, wherein said further amount of electrolyte is provided by an excess of the same electrolyte used to form the viscoelastic surfactant.

21. A method as claimed in Claim 19 or Claim 20, wherein said further amount of electrolyte is 0.5 to 5 moles per mole of surfactant ions.

22. A method as claimed in any one of the preceding claims, wherein the bleach composition comprises from 0.5 to 50 percent bleaching agent and from 50 to 99.5 percent aqueous liquid, both percentages based on the weight of the bleach composition.

23. An aqueous bleach composition thickened by a viscoelastic surfactant according to the method of any one of Claims 1 to 16.

Revendications

1. Procédé d'épaississement d'une composition aqueuse de blanchiment contenant un agent de blanchiment, qui consiste à former en son sein un agent tensioactif viscoélastique en mettant la composition en contact avec une quantité efficace d'un ion tensioactif possédant un fragment hydrophobe chimiquement lié à un fragment hydrophile ionique et d'un électrolyte possédant un fragment qui s'associe avec l'ion tensioactif pour former un agent tensioactif viscoélastique, et, éventuellement, à épaissir encore la composition de blanchiment et/ou augmenter la stabilité de sa viscosité à des températures relativement élevées, en y ajoutant une quantité supplémentaire d'un électrolyte possédant un fragment qui s'associe à l'ion tensioactif.

2. Procédé tel que revendiqué dans la revendication 1, dans lequel ledit agent tensioactif viscoélastique est représenté par la formule:



dans laquelle $R_1(Y^{\circ})$ et $R_1(Z^{\circ})$ représentent des ions tensioactifs, R_1 est un fragment hydrophobe, Y° est un fragment hydrophile cationique solubilisant, chimiquement lié à R_1 , Z° est un fragment hydrophile anionique solubilisant, chimiquement lié à R_1 , X° est un contre-ion associé à Y° , et A° est un contre-ion associé à Z° .

3. Procédé tel que revendiqué dans la revendication 2, dans lequel l'ion tensioactif est représenté par la formule



dans laquelle R_1 et X° ont les définitions données dans la revendication 2, et Y° est un ion onium.

4. Procédé tel que revendiqué dans la revendication 3, dans lequel Y° est choisi parmi les groupes ammonium quaternaire, sulfonium et phosphonium.

5. Procédé tel que revendiqué dans la revendication 4, dans lequel Y° est un groupe ammonium quaternaire de formule $N^{\oplus}(R)_3$, dans laquelle chaque R est méthyle ou éthyle.

6. Procédé tel que revendiqué dans la revendication 2, dans lequel l'ion tensioactif est représenté par la formule



dans laquelle R_1 et A° ont les définitions données dans la revendication 2, et Z° est choisi parmi des

groupes sulfate, des groupes éther-sulfate, des groupes sulfonate, des groupes carboxylate, des groupes phosphate et des groupes phosphonate.

- 5 7. Procédé tel que revendiqué dans la revendication 6, dans lequel Z^e est choisi parmi des groupes carboxylate et des groupes sulfate.
8. Procédé tel que revendiqué dans l'une quelconque des revendications 2 à 7, dans lequel R₁ représente un groupe alkyle en C₁₄₋₂₄.
- 10 9. Procédé tel que revendiqué dans la revendication 8, dans lequel ledit ion tensioactif est choisi parmi cétyltriméthylammonium, myristyltriméthylammonium et stéaryltriméthylammonium.
- 15 10. Procédé tel que revendiqué dans l'une quelconque des revendications précédentes, dans lequel le fragment hydrophobe contient un groupe fluoroaliphatique.
11. Procédé tel que revendiqué dans la revendication 10, dans lequel ledit groupe fluoroaliphatique est un groupe perfluoroaliphatique linéaire, représenté par la formule C_nF_{2n+1}, dans laquelle n vaut de 3 à 10.
- 20 12. Procédé tel que revendiqué dans l'une quelconque des revendications 1 à 5 et 8 à 11, dans lequel le contreion associé à l'ion tensioactif, dans l'agent tensioactif viscoélastique, est un sulfonate ou un carboxylate.
13. Procédé tel que revendiqué dans la revendication 12, dans lequel le contre-ion est un sulfonate aromatique.
- 25 14. Procédé tel que revendiqué dans la revendication 13, dans lequel l'agent tensioactif viscoélastique est représenté par la formule

$$\text{CH}_3(\text{CH}_2)_n\text{-N}^+(\text{R})_3 \text{X}^e,$$
 30 dans laquelle n vaut de 13 à 23, chaque R représentant, indépendamment l'un de l'autre, un groupe alkyle ou alkylaryle, et X^e est le groupe p-toluènesulfonate.
- 35 15. Procédé tel que revendiqué dans l'une quelconque des revendications 1, 2 et 6 à 11, dans lequel le contreion associé à l'ion tensioactif, dans l'agent tensioactif viscoélastique, est un ion onium.
16. Procédé tel que revendiqué dans la revendication 15, dans lequel le contre-ion est un groupe ammonium quaternaire.
- 40 17. Procédé tel que revendiqué dans l'une quelconque des revendications précédentes, dans lequel ledit agent tensioactif viscoélastique est présent en une proportion valant de 0,05 à 10 % en poids de la composition de blanchiment.
- 45 18. Procédé tel que revendiqué dans la revendication 17, dans lequel ladite proportion vaut de 0,1 & 2 % en poids.
19. Procédé tel que revendiqué dans l'une quelconque des revendications précédentes, dans lequel ladite proportion supplémentaire facultative d'électrolyte est ajoutée à la composition de blanchiment contenant l'agent tensioactif viscoélastique.
- 50 20. Procédé tel que revendiqué dans la revendication 19, dans lequel ladite proportion supplémentaire d'électrolyte est fournie par un excès du même électrolyte utilisé pour former l'agent tensioactif viscoélastique.
- 55 21. Procédé tel que revendiqué dans la revendication 19, dans lequel ladite proportion supplémentaire d'électrolyte est de 0,5 à 5 mole(s) par mole d'ions tensioactifs.
22. Procédé tel que revendiqué dans l'une quelconque des revendications précédentes, dans lequel ladite

composition de blanchiment comprend de 0,5 & 50 % d'agent de blanchiment et de 50 à 99,5 % de liquide aqueux, les deux pourcentages étant rapportés au poids de la composition de blanchiment.

23. Composition aqueuse de blanchiment, épaissie par un agent tensioactif viscoélastique selon le procédé de l'une quelconque des revendications 1 à 16.

Patentansprüche

1. Verfahren zum Verdicken einer wäßrigen, ein Bleichmittel enthaltenden Bleichzusammensetzung durch Ausbilden eines viscoelastischen, oberflächenaktiven Mittels darin, durch Inberührungbringen der Zusammensetzung mit einer wirksamen Menge eines Ions eines oberflächenaktiven Mittels, das eine hydrophobe Gruppe aufweist, die chemisch an eine ionische hydrophile Gruppe gebunden ist, und einen Elektrolyten, der eine Gruppe aufweist, die sich mit dem Ion des oberflächenaktiven Mittels verbindet, um ein viscoelastisches, oberflächenaktives Mittel auszubilden, und gegebenenfalls weiteres Verdicken der Bleichzusammensetzung und/oder Erhöhen ihrer Viskositätsstabilität bei höheren Temperaturen durch Zugabe einer weiteren Menge eines Elektrolyten, der eine Gruppe aufweist, die sich mit dem Ion des oberflächenaktiven Mittels verbindet.
2. Verfahren nach Anspruch 1, **dadurch gekennzeichnet**, daß das viscoelastische, oberflächenaktive Mittel der Formel genügt $R(Y^{\circ})X^{\circ}$ oder $R(Z^{\circ})A^{\circ}$, in der R (Y°) und R_1 (Z°) Ionen oberflächenaktiver Mittel sind, R_1 eine hydrophobe Gruppe ist, Y° ist eine kationische, solubilisierende hydrophile Gruppe, chemisch an R_1 gebunden, Z° ist eine anionische, solubilisierende hydrophile Gruppe, chemisch an R_1 gebunden, X° ist ein mit Y° verbundenes Gegenion und A° ist ein mit Z° verbundenes Gegenion.
3. Verfahren nach Anspruch 2, **dadurch gekennzeichnet**, daß das Ion des oberflächenaktiven Mittels der Formel genügt $R_1(Y^{\circ})X^{\circ}$, in der R_1 und X° die in Anspruch 2 angegebene Bedeutung haben und Y° ein Oniumion ist.
4. Verfahren nach Anspruch 3, **dadurch gekennzeichnet**, daß Y° ausgewählt ist aus quartären Ammonium-, Sulfonium und Phosphoniumgruppen.
5. Verfahren nach Anspruch 4, **dadurch gekennzeichnet**, daß Y° eine quartäre Ammoniumgruppe der Formel $N^{\circ}(R)_3$ ist, in der jedes R Methyl oder Ethyl ist.
6. Verfahren nach Anspruch 2, **dadurch gekennzeichnet**, daß das Ion des oberflächenaktiven Mittels der Formel genügt $R_1(Z^{\circ})A^{\circ}$, in der R_1 und A° die in Anspruch 2 angegebene Bedeutung haben und Z° ausgewählt ist aus Sulfatgruppen, Ethersulfatgruppen, Sulfonatgruppen, Carboxylatgruppen, Phosphatgruppen und Phosphonatgruppen.
7. Verfahren nach Anspruch 6, **dadurch gekennzeichnet**, daß Z° aus Carboxylatgruppen und Sulfatgruppen ausgewählt ist.
8. Verfahren nach jedem der Ansprüche 2-7, **dadurch gekennzeichnet**, daß R_1 eine C_{14} - C_{24} -Alkylgruppe ist.
9. Verfahren nach Anspruch 8, **dadurch gekennzeichnet**, daß das Ion des oberflächenaktiven Mittels aus Cetyltrimethylammonium, Myristyltrimethylammonium und Stearyltrimethylammonium ausgewählt ist.

10. Verfahren nach jedem der vorstehenden Ansprüche,
dadurch gekennzeichnet,
daß die hydrophobe Gruppe eine fluoraliphatische Gruppe enthält.
- 5 11. Verfahren nach Anspruch 10,
dadurch gekennzeichnet,
daß die fluoraliphatische Gruppe eine lineare perfluoraliphatische Gruppe der Formel C_nF_{2n+1} ist, in der n 3-10 ist.
- 10 12. Verfahren nach jedem der Ansprüche 1-5 und 8-11,
dadurch gekennzeichnet,
daß das Gegenion zum Ion des oberflächekoaktiven Mittels in dem viscoelastischen, oberflächenaktiven Mittel ein Sulfonat oder Carboxylat ist.
- 15 13. Verfahren nach Anspruch 12,
dadurch gekennzeichnet,
daß das Gegenion ein aromatisches Sulfonat ist.
- 20 14. Verfahren nach Anspruch 13,
dadurch gekennzeichnet,
daß das viscoelastische, oberflächenaktive Mittel der Formel genügt $CH_3-(CH_2)_n-N^+(R)_3X^\ominus$, in der n 13-23 ist, jedes R unabhängig Alkyl oder Alkylaryl ist und X^\ominus para-Toluolsulfonat ist.
- 25 15. Verfahren nach jedem der Ansprüche 1, 2 und 6-11,
dadurch gekennzeichnet,
daß das Gegenion des Ions des oberflächenaktiven Mittels im viscoelastischen, oberflächenaktiven Mittel ein Oniumion ist.
- 30 16. Verfahren nach Anspruch 15,
dadurch gekennzeichnet,
daß das Gegenion eine quartäre Ammoniumgruppe ist.
- 35 17. Verfahren nach jedem der vorstehenden Ansprüche,
dadurch gekennzeichnet,
daß das viscoelastische, oberflächenaktive Mittel in einer Menge von 0,05-10 Gew.-%, bezogen auf das Gewicht der Bleichzusammensetzung, vorhanden ist.
- 40 18. Verfahren nach Anspruch 17,
dadurch gekennzeichnet,
daß die Menge 0,1-2 Gew.-% beträgt.
- 45 19. Verfahren nach jedem der vorstehenden Ansprüche,
dadurch gekennzeichnet,
daß gegebenenfalls eine weitere Elektrolytmenge zu der das viscoelastische, oberflächenaktive Mittel enthaltenden Bleichzusammensetzung zugegeben wird.
- 50 20. Verfahren nach Anspruch 19,
dadurch gekennzeichnet,
daß die weitere Menge des Elektrolyten geschaffen ist durch einen Überschuß des gleichen Elektrolyten, der zur Bildung des viscoelastischen, oberflächenaktiven Mittels verwendet wurde.
- 55 21. Verfahren nach Anspruch 19 oder Anspruch 20,
dadurch gekennzeichnet,
daß die weitere Menge Elektrolyt 0,5-5 Mole pro Mol Ionen des oberflächenaktiven Mittels sind.
22. Verfahren nach jedem der vorstehenden Ansprüche,
dadurch gekennzeichnet,
daß die Bleichzusammensetzung von 0,5-50% Bleichmittel und von 50-99,5% wäßrige Flüssigkeit

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enthält, wobei beide Prozentangaben sich auf Gewicht der Bleichzusammensetzung beziehen.

- 23.** Wäßrige Bleichzusammensetzung, verdickt durch in viscoelastisches, oberfläch naktives Mittel nach dem Verfahren von jedem der Ansprüche 1-16.

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